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by

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THE THERMODYNAMIC TEMPERATURE SCALE BELOW 90°K

THE NORMAL BOILING POINT OF NORMAL HYDROGEN*

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In a previous communication [1] we have reported a new value for the normal boiling point of oxygen on the thermodynamic scale for 0°C = 273.16°K. The value of 90.154° ± 0.005°K. is 0.04°K. lower than the Reichsanstalt values.[2,a,b]

1. J. G. Aston and G. W. Moessen, J. Chem. Phys, 21, 948 (1953)

2a. W. Heuse and J. Otto, Ann Physik 9, 486, (1931)
2b. W. Heuse and J. Otto, Ann Physik 14, 185, (1932)

The general method and accuracy of our gas thermometry between 10°K. and 90°K. was also briefly mentioned at the same time.[1] It will be a few months before full details and values will be available for our temperature scale below 90°K. at ice point pressures of 1.0 m., 1.8 m., and 2.7 m. However, well spaced points between 10°K. and 50°K, with a demonstration of the adequacy of the virial coefficients by a comparison of the result at 20°K. at the three ice point pressures have been com-

pletely calculated. Since one of the platinum thermometers compared with our gas thermometer was a N.B.S. secondary standard, a comparison of our new Scale with that of the National Bureau of Standards is possible. As far as we are aware this is the first time agreement has been established between two independent Scales below 90°K. within the claimed accuracy. The extraordinary agreement together with the fact that we can now report a new value for the normal boiling point of normal hydrogen which also allows comparison with the Leiden Scale prompts us to make available our results to date.

Table 1 reports the difference between our Scale and that of the N.B.S. [3]

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3. H. J. Hoge and Ferdinand G. Brickwedde, J. Research Nalt. Bur. Standards, 22, 351 (1939)

The approximate temperature is given in column 1 and the approximate ice point pressure is given in column 2. The difference between our value and the value actually reported by the N.B.S. for a Scale which was believed to correspond to an ice point temperature of 273.16°K. is given in column 3. However, they actually used the oxygen normal boiling point as their reference point and assigned to it the value of 90.19°K. If we accept our new value of 90.154°K. for the normal boiling point of oxygen, the N.B.S. Scale actually corresponds to an ice point temperature of 273.27°K. In column 4 the difference between our value and the value on the N.B.S. Scale corrected to our normal boiling point of oxygen is given. Inasmuch as Hoge and Brickwedde had a sensitivity of about 0.015° in reading their pressures, an accuracy of 0.02° was claimed although the average accuracy should be better. The agreement is excellent.

Table II tabulates our values for the normal boiling point of normal hydrogen obtained by introduction of liquid normal hydrogen directly into the gas thermometer apparatus approximately one year after the helium gas thermometry measurements. Platinum thermometers Pt-G8 and Pt-G12 were never removed from the original assembly.

The results were corrected for ortho-para conversion using the data of Keesom, Bijl, and Van der Horst [4] for liquid normal hydrogen in glass.

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4. Keesom, Bijl and Miss Van der Horst, Leiden Commun, no. 217a (1931)

The data were derived from the measurements of equilibrium temperatures with Pt-G8 and Pt-G12 at the pressures noted in column 1. Correction to 760 mm. was made using equation 1.

$$\Theta = -252.754 + 0.00441\ (p-760) - 5.0 \times 10^{-6}\ (p-760)^2 \quad (1)$$

in this equation, Θ is in degrees centigrade thermodynamic scale. Column 1 gives the equilibrium pressure, while columns 2 and 3 give the normal boiling points computed from the resistance of Pt-G8 and Pt-G12 respectively and corrected to 760 mm using equation 1. The average for each of the thermometers is compared with a value given below which was obtained by interpolating the observed equilibrium temperatures on each thermometer to 760 mm pressure.

Table III summarizes values for the normal boiling point of normal hydrogen corrected to an ice point temperature of 273.16°K. by conventional methods.

The average of all values not including our own since 1913 is 20.378°K. The average of all values not including our own since 1931 is 20.379°K. The average of our two values obtained by linear interpolation (using the form log p versus 1/T) is 20.365° ± .01°K. The lower accuracy of 0.01° is dictated by the correction for ortho-para conversion which amounted to 0.012°. If we exclude the N.B.S. value because of the lower sensitivity and average the value of Heuse and Otto, the value of Keesom, Bijl, and Miss Van der Horst and our own value, the average is 20.374°K. It is of interest to note that if the N.B.S. value for the normal boiling point of normal hydrogen is placed on our new Scale (as determined from intercomparison of the N.B.S. platinum thermometer with our gas thermometry measurements) the agreement with our recent value for this fixed point is nearly exact. This also indicates that the

uncertainty of ± 0.01° we assigned to our value of 20.365°K. is conservative. Referred to 273.16°K. as the thermodynamic temperature of the ice point, it is recommended that, until our own value of 20.365°K. be confirmed, that 20.37 ± .01°K. be used as the normal boiling point of normal hydrogen in view of the high values measured between 1917 and 1924 both at Leiden and at the Reichsanstalt. It would seem that no value as high as 20.39°K. is admissable.

Table I

Comparison of Penn State and N.B.S. Thermodynamic Temperature Scales Below 90°K.

March and April, 1951

T	P_o(m.)	Δ_1 (NBS_{orig} - PSC)	Δ_2 (NBS_{corr} - PSC)
10.5	2.7	$+0.058_9 \pm 0.01$	$+0.054_8$
15.0	1.8	$+0.017_1$	$+0.011_0$
20.3	1.0	$+0.025_4$	$+0.017_3$
20.3	1.8	$+0.026_0$	$+0.017_9$
20.3	2.7	$+0.020_6$	$+0.012_5$
25.0	1.8	$+0.023_0$	$+0.012_9$
33.0	2.7	$+0.027_6$	$+0.014_3$
40.0	2.7	$+0.022_0$	$+0.005_9$
49.7	1.0	$+0.017_8$	-0.002_2

Table II

Temperatures Corresponding to the Normal Boiling Point of Normal Hydrogen on the New Penn State Thermodynamic Scale.

Deduced from Equation 1 ; $0^{\circ}C = 273.16^{\circ}K$.

March 30, 1952

Pressure	Pt-G8	Pt-G12	Average
735.283 mm	$20.366^{\circ}K$	$20.367^{\circ}K$	$20.367^{\circ}K$
748.371	20.364°	20.364°	20.364°
773.979	20.364°	20.365°	20.365°
Average	$20.365^{\circ}K$	$20.365^{\circ}K$	$20.365^{\circ}K$
Interpolated	$20.364^{\circ}K$	$20.365^{\circ}K$	$20.365^{\circ}K$

Table III

Various Values Reported for the Normal Boiling Point of Normal Hydrogen

Date	Investigators	Temp Reported	To Used	Temp, °K corrected to T_o = 273.160°K.
1913	Onnes and Keesom [5]	20.35°K	273.09°	20.36°
1914	(PTR) Henning [6]	-252.79°C	273.10°	20.31°
1917	Cath and Onnes [7]	20.39°K	273.09°	20.40°
1922	Martinez and Onnes [8]	20.35_2°K	273.09°	20.35_7°
1924	Henning and Heuse [9]	-252.78_9°C	273.20°	20.41_4°
1927	Henning [10]	20.43°K	273.20°	20.43°
1931	Heuse and Otto [2a]	-252.780°C	273.16°	20.380°
1931	Keesom, Bijl and Van der Horst [4]	-252.754°C	273.13	20.376°
1939	Hoge and Brickwedde [3]	20.39°K	273.16	20.38° *
1952	This Research	20.365°K	273.16	20.365°

5. H. K. Onnes and W. H. Keesom: Leiden Commun. no. 137d (1913) and later recomputed by P. G. Cath and H. K. Onnes: Leiden Commun. no. 152a (1917)
6. Physickalisch-technische Reichsanstalt: Zs. fur Instrumentenk., 35, 174 (1915)
7. P. G. Cath and H. K. Onnes: Leiden Commun. no. 152a (1917)
8. J. P. Martinez and H. K. Onnes: Leiden Commun no. 156b (1922)
9. F. Henning and W. Heuse Zs. fur Physik, 23, 105 (1924)
10. F. Henning: Zs. fur Physick, 40, 775 (1927)

* Corrected to oxygen point of 90.154°K. as explained in text.